



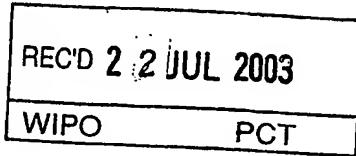
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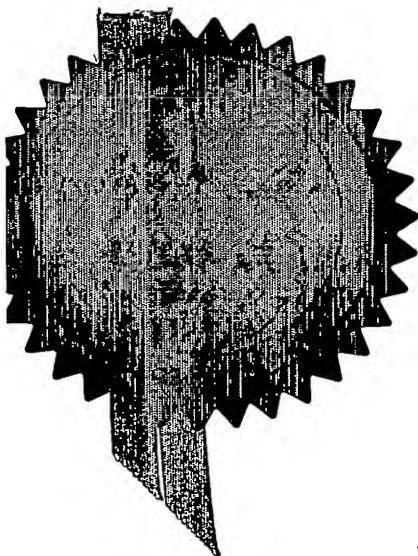


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22JUL02 E735003-1 D10149

P01/77000 01/00 2002 169407

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1. Your reference

30060 P1

0216940.7

2. Patent application number

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20 JUL 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

 Givaudan SA
 Chemin de la Parfumerie 5
 1214 Vernier
 Switzerland

Patents ADP Number (if you know it)

8408031 001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the Invention

Improvements in or relating to organic compounds

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

 CIT Givaudan UK Ltd.
 Magna House
 76-80 Church Street
 Staines, Middlesex TW18 4XR, England

Patents ADP number (if you know it)

8408056 001

5. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

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Date of filing (day/month/year)

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Number of earlier application

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Description 17

Claim(s) 2

Abstract 1

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Colin Brown (office time) Tel. No: 01/784417721

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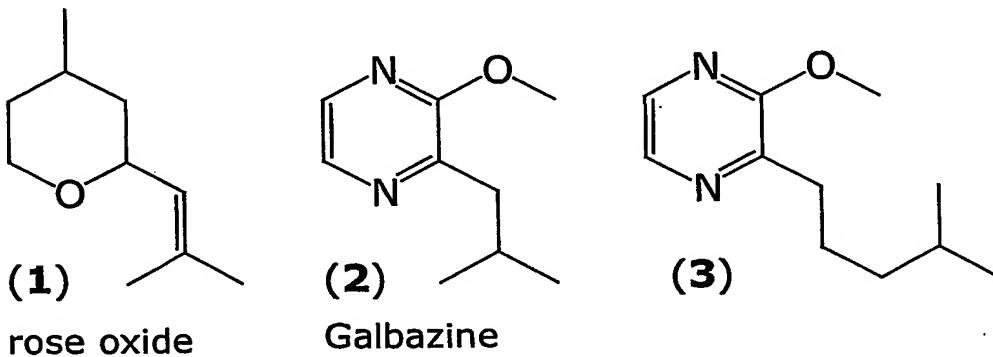
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Improvements in or relating to organic compounds

The invention is concerned with new fragrance ingredients, their manufacture and use in fragrance compositions, particularly in fine 5 perfumery and cosmetics compositions.

During their investigations of the low-boiling constituents of Bulgarian rose oil in 1959, C. F. Seidel and M. Stoll (*Helv. Chim. Acta* 1959, 42, 1830) discovered an important trace constituent of green-metallic odor reminiscent of geranium oil and carrot leaves. They termed this new odorant rose oxide 10 and later attributed it the structure 1 (C.F. Seidel, D. Felix, A. Eschenmoser, K. Biemann, E. Palluy, M. Stoll, *Helv. Chim. Acta* 1961, 44, 598). Though in substance the very powerful, green-metallic odor of rose oxide is rather unpleasant, today it is extensively used in many fragrances to provide diffusivity, lift and naturalness, especially in the top note of perfumes.



15

The methoxy pyrazines 2 and 3 represent another class of very powerful green odorants. 2 was first discovered by R. G. Buttery et al. in green bell pepper oil (R. G. Buttery, R. M. Seifert, R. E. Lundin, D. G. Guadagni, L. C. 20 Ling, *Chem. Ind.* 1969, 490) and later also found in galbanum oil (A. F. Bramwell, J. W. K. Burrell, G. Riezebos, *Tetrahedron Lett.* 1969, 3215). It is reminiscent of peperoni, galbanum oil and green peas, and has been introduced into perfumery successfully as Galbazine®. Isohexyl methoxy pyrazine (3) with its more pleasant green, vegetable and hyazinth odor is also

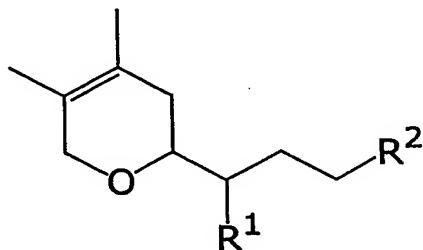
frequently used in perfumery, though in very low concentration due to its exceptional strength. Yet, even in high dilutions, all these pyrazines have harsh, unpleasant by-odors, which limit their use in perfumery.

Unfortunately, blending of the aforementioned materials has not lead
5 to any interesting odor tonalities without harsh, unpleasant or metallic-
burnt aspects being noticeable.

Accordingly, there is a need to provide new ingredients to develop
interesting odor tonalities that have proven inaccessible by simple blending
of these known compounds.

10 Surprisingly, we have now found certain 3,6-dihydro-2H-pyrans, which possess the characteristic odor notes of methoxy pyrazines, but do not exhibit the harsh by-notes that prohibit the extensive use of these pyrazines in perfumery. Facettes of rose oxides are also present in these compounds leading to overall interesting, novel odor tonalities.

15 Therefore, the invention provides in a first aspect a compound of the general formula (I),



20 wherein $R^1 = H, CH_3$ or CH_2CH_3 ,
and $R^2 = H, CH_3, CH_2CH_3$ or $CH_2CH_2CH_3$, provided that
when R^1 is H , R^2 is H .

25 The compounds of formula (I) may comprise more than one chiral centre and as such they may exist as a mixture of enantiomers and diastereomers, or they may be resolved as enantiomerically and

diastereomerically pure forms. However, resolving stereoisomers adds to the complexity of manufacture and purification of these compounds and so it is preferred to use a compound of formula (I) as a mixture of its stereoisomers simply for economic reasons. However, if it is desired to prepare pure 5 stereoisomers, this may be achieved according to methodology known in the art.

Compounds of formula (I) may be prepared according to techniques known in the art using commercially available starting materials, or materials that can be easily prepared from known starting materials. The 10 compounds may be prepared according to a retro-Diels-Alder reaction using 2,3-dimethyl-1,3-butadiene and an appropriately substituted aldehyde, for example butyraldehyde may be employed in the formation of compound (7) in Table 1. Reaction conditions for these Diels Alder reactions are more fully described in the Examples set forth below. The skilled person will appreciate 15 that other compounds of the present invention may be prepared using an appropriately substituted aldehyde.

In another aspect of the present invention there is provided the use of a compound of the general formula (I) or mixtures thereof as a fragrance ingredient wherein,

20 $R^1 = H, CH_3$ or CH_2CH_3 , and
 $R^2 = H, CH_3, CH_2CH_3$ or $CH_2CH_2CH_3$.

Compounds described hereinabove possess unique, character-donating aspects that makes them suitable for a broad range of possible applications in perfumery. Furthermore, because the compounds do not 25 possess the harsh unpleasant by-notes of the pyrazines exemplified by (2) and (3) above, they may confer a fresh green touch to virtually all kinds of perfume compositions, in virtually all kinds of applications from fine fragrances to cosmetics and detergents, e.g. in shampoos, skin-care products or soaps. Depending on the dosage, the effects can reach from providing more 30 naturalness and character to building up hyazinth or petigrain or other green accords. The use is neither limited to any type of perfume nor to any special

olfactory directions, odorants or classes of substances. A few illustrative examples of classes of substances, which harmonize equally well are:

- ethereal oils and extracts, e.g. angelica oil, basilic oil, bergamot oil, 5 carrot seed oil, citrus oils, coriander oil, galbanum oil, geranium oil, jasmin absolute, neroli oil, orris oil, petitgrain oil, rose oil, or violet leaf oil;
- alcohols, e.g. citronellol, cinnamic alcohol, dihydromyrcenol, Ebanol°, 10 Florol°, geraniol, linalool, Mayol°, phenylethyl alcohol or terpineol ;
- aldehydes and ketones, e.g. decanal, *alpha*-hexylcinnamaldehyd, hydroxy-citronellal, isoeugenol, Iso E Super°, Isoraldeine°, Hedione°, methylionone or vanillin; 15
- ether and acetals, e.g. Ambrox°, 2-(1-ethoxyethoxy)ethyl benzene, geranyl methyl ether, Magnolan°, 2-(1-propoxyethoxy)ethyl benzene, or rose oxide (1).
- 20 - esters and lactones, e.g. benzyl acetat, benzyl salicylate, coumarin, γ -decalactone, ethylene brassylate, Thibetolide°, γ -undecalactone.
- heterocycles, e.g. indol, Galbazine (2) or 6-/8-isobutylchinoline.

25 Compounds of formula (I) that are particularly preferred for their fragrance properties are set forth in Table 1.

Table 1. Compounds of general formula (I) having R¹ and R² as indicated

Compound	R ¹	R ²
4	H	Methyl
5	H	Ethyl
6	H	Propyl
7	H	H
8	Ethyl	H
9	Methyl	H
10	Methyl	Methyl

Having regard to compounds in Table 1, compound 4, compound 5 and compound 6 are known compounds, however, the olfactive properties of these compounds have not been previously disclosed.

Compounds according to the formula (I) may be employed in any of the fragrance compositions referred to above in widely varying amounts having regard to the other fragrance ingredients employed and depending on the fragrance accord that a perfumer is trying to achieve. Generally however, one may employ about 0.01 to 1.0% by weight in fine fragrances and about 0.01 to 10% by weight in other perfumed products.

In addition to their admixture with other fragrance ingredients, the compounds of formula (I) may be admixed with one or more excipients conventionally used in conjunction with fragrances in fragrance compositions, for example carrier materials, and other auxiliary agents commonly used in the art such as solvents, preservatives, colourants and the like.

The invention is now illustrated with reference to the following examples.

Examples

4,5-Dimethyl-2-propyl-3,6-dihydro-2H-pyran (Compound 7):

2-Nitropropane (1.8 ml, 20 mmol) was added at 0 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (50 ml). A 5 solution of butanal (14.4 g, 200 mmol) in dichloromethane (30 ml) was added, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) at 0 °C. After stirring for 3h at this temperature, and for 1h at ambient 10 temperature, the reaction mixture was poured into water (400 ml) and the product extracted with pentane (3x 300 ml). The combined organic extracts were dried, concentrated in vacuo, and purified by silica-gel FC (pentane/MTBE, 99:1) to provide the title compound 7 (3.55 g, 12%).

Odor: green, spicy, rose oxide, vegetable. – IR (neat): $\nu = 1098 \text{ cm}^{-1}$ ($\nu \text{ C}-\text{O}-\text{C}$), 1386 ($\delta \text{ CH}_3$), 1449 ($\delta \text{ CH}_2$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.93$ (t, $J = 7.0 \text{ Hz}$, 3H, 5'- H_3), 1.34–1.57 (m, 4H, 1'- H_2 –2'- H_2), 1.53 / 1.63 (2s, 6H, 4-,5-Me), 1.80 (d, $J = 16.5 \text{ Hz}$, 1H, 3- H_b), 1.93 (br. t, $J = 16.5 \text{ Hz}$, 1H, 3- H_a), 3.47 (m, 1H, 2-H), 3.93 / 4.01 (2d, $J = 15.5 \text{ Hz}$, 2H, 6- H_2). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 13.8$ (q, 5-Me), 14.1 (q, C-3'), 18.3 (q, 4-Me), 18.6 (C-2'), 36.7 (t, C-3), 38.0 (t, C-1'), 69.8 (t, C-6), 73.9 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (45) [C_3H_5^+], 55 (55) [C_4H_7^+], 67 (100) [C₅H₇⁺], 82 (99) [C₆H₁₀⁺], 111 (19) [M⁺–C₃H₇], 139 (21) [M⁺–CH₃], 154 (67) [M⁺].

2-(1-Ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 8):

25 2-Nitropropane (1.8 ml, 20 mmol) was added at –10 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, 2-ethylbutanal (20.0 g, 200 mmol) was added dropwise during 20 min, followed by 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) during 30 min. After further stirring at this temperature for 30 min, and for 30 1h at ambient temperature, the reaction mixture was poured into water (300 ml) and the product extracted with MTBE (3x 300 ml). The combined organic

extracts were dried, concentrated in *vacuo*, and purified by silica-gel FC (pentane/MTBE, 100:1, R_f = 0.47) to provide the title compound 8 (5.53 g, 15%).

Odor: green, carrot leaves, rose oxide, metallic, green peas, galbanum. – IR (neat): ν = 1099 cm^{-1} (ν C–O–C), 1384 (δ CH₃), 1461 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.88 (t, J = 7.5 Hz, 6H, 3'-,2''-H₂), 1.53 / 1.64 (2s, 6H, 4-,5-Me), 1.19–1.50 (m, 5H, 1'-H, 2'-,1''-H₂), 1.74 (br. d, J = 16.0 Hz, 1H, 3-H_b), 2.03 (br. t, J = 16.0, 1H, 3-H_a), 3.41 (m_c, 1H, 2-H), 3.93 / 3.99 (2d, J = 15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 11.2 / 11.3 (2q, C-3',-2''), 13.7 (q, 5-Me), 18.4 (q, 4-Me), 21.2 / 21.3 (2t, C-2',-5). – MS (EI): *m/z* (%) = 41 (45) [C₃H₅⁺], 55 (54) [C₄H₇⁺], 67 (66) [C₅H₇⁺], 83 (100) [C₆H₁₁⁺], 111 (65) [M⁺–C₅H₁₁], 182 (28) [M⁺].

15 **2-Butyl-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 4):**

2-Nitropropane (1.8 ml, 20 mmol) was added at 0 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). Pentanal (17.2 g, 200 mmol) was added at –78 °C, followed by 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol). The cooling bath was removed and the reaction was stirred at room temperature for 3h. The mixture was then poured into water (400 ml), and the product extracted with pentane (3x 400 ml). The organic extracts were combined and dried, the solvent was evaporated in *vacuo*, and the resulting residue purified by distillation to furnish at 34–38 °C / 0.05 mbar the title compound 4 (7.87 g, 12%).

Odor: green, spicy, rose oxide, hyazinth. – IR (neat): ν = 1100 cm^{-1} (ν C–O–C), 1387 (δ CH₃), 1450 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.91 (t, J = 7.0 Hz, 3H, 5'-H₃), 1.30–1.58 (m, 6H, 1'-H₂–3'-H₂), 1.53 / 1.63 (2s, 6H, 4-,5-Me), 1.80 (d, J = 16.0 Hz, 1H, 3-H_b), 1.94 (br. t, J = 16.0 Hz, 1H, 3-H_a), 3.45 (m_c, 1H, 2-H), 3.93 / 4.01 (2d, J =

15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 13.8 (q, 5-Me), 14.0 (q, C-4'), 18.3 (q, 4-Me), 22.7 (t, C-3'), 27.7 (t, C-2'), 35.6 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.2 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): *m/z* (%) = 41 (36) [C₃H₅⁺], 55 (41) [C₄H₇⁺], 67 (79) [C₅H₇⁺], 82 (100) [C₆H₁₀⁺], 85 (58) [C₅H₉O⁺], 111 (20) [M⁺–C₄H₉], 153 (16) 5 [M⁺–CH₃], 168 (54) [M⁺].

4,5-Dimethyl-2-pentyl-3,6-dihydro-2H-pyran (Compound 5):

10 2-Nitropropane (1.8 ml, 20 mmol) was added at –10 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, a solution of hexanal (20.0 g, 200 mmol) in dichloromethane (80 ml) was added within 15 min, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) in a period of 15 another 15 min. After further stirring at 0 °C for 90 min, the cooling bath was removed, and another portion of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) was added dropwise with stirring at room. Stirring was continued at ambient temperature for 14 h, prior to pouring the reaction mixture into water (400 ml) and extraction of the product with MTBE (3x 400 ml). The 20 combined organic extracts were dried, the solvent was removed under reduced pressure, and the resulting residue purified by distillation in vacuo to provide at 53–58 °C / 0.30–0.35 mbar the title compound 5 (5.41 g, 15%).

25 Odor: Strong, green peas, vegetable, isohexyl methoxy pyrazine, lily and hyazinth. – IR (neat): ν = 1102 cm⁻¹ (ν C–O–C), 1386 (δ CH₃), 1449 (δ CH₂), 1691 (ν C=C). – ¹H-NMR (CDCl₃): δ = 0.89 (t, *J* = 7.0 Hz, 3H, 5'-H_a), 1.27–1.69 (m, 8H, 1'-H₂–4'-H₂), 1.53 / 1.59 (2s, 6H, 4-,5-Me), 1.80 (d, *J* = 16.0 Hz, 1H, 3-H_b), 1.94 (br. t, *J* = 16.0 Hz, 1H, 3-H_a), 3.45 (m, 1H, 2-H), 3.93 / 4.01 (2d, *J* = 15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 13.8 (q, 5-Me), 14.0 (q, C-5'), 18.3 (q, 4-Me), 22.6 (t, C-4'), 30 25.1 (t, C-2'), 31.9 (t, C-3'), 35.8 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.2 (d, C-2), 123.5 /

124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (32) [$C_3H_5^+$], 55 (38) [$C_4H_7^+$], 67 (64) [$C_5H_7^+$], 82 (100) [$C_6H_{10}^+$], 111 (20) [$M^+-C_5H_{11}$], 167 (11) [M^+-CH_3], 182 (37) [M^+].

5

2-Hexyl-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 6):

2-Nitropropane (1.8 ml, 20 mmol) was added at -10°C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml).
 10 Heptanal (22.8 g, 200 mmol) was added dropwise at this temperature during 15 min, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) during 20 min. The reaction was stirred -10°C for 15 min., and at room temperature for 1h. Another portion of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) was added during 20 min, and stirring was continued at
 15 room temperature for 15 h. The mixture was then poured into water (300 ml), and the product extracted with MTBE (3x 300 ml). The organic extracts were combined and dried, the solvent was evaporated in vacuo, and the resulting residue purified by FC (pentane/ether, 100:1) on silica gel to provide the title compound 6 (2.78 g, 7%).

20

Odor: Strong, green peas, parsley, vegetable, pyrazine, roots. – IR (neat): ν = 1104 cm^{-1} (ν C–O–C), 1456 (δ CH_2), 1386 (δ CH_3), 1693 (ν C=C). – $^1\text{H-NMR}$ ($CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3H, 6'- H_3), 1.29–1.69 (m, 10H, 1'- H_2 –5'- H_2), 1.53 / 1.63 (2s, 6H, 4,-5-Me), 1.80 (d, J = 16.0 Hz, 1H, 3- H_b), 1.94 (br. t, J = 16.0 Hz, 1H, 3- H_a), 3.45 (m, 1H, 2-H), 3.93 / 4.01 (2d, J = 16.0 Hz, 2H, 6- H_2). – $^{13}\text{C-NMR}$ ($CDCl_3$): δ = 13.8 (q, 5-Me), 14.1 (q, C-6'), 18.3 (q, 4-Me), 22.6 (t, C-5'), 25.4 (t, C-2'), 29.4 (t, C-3'), 31.8 (t, C-4'), 35.9 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.3 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (24) [$C_3H_5^+$], 55 (29) [$C_4H_7^+$], 67 (51) [$C_5H_7^+$], 82 (100) [$C_6H_{10}^+$], 85 (52) [$C_6H_{13}^+$], 111 (21) [$M^+-C_6H_{13}$], 181 (13) 30 [M^+-CH_3], 196 (37) [M^+].

4,5-Dimethyl-2-(1-methylpropyl)-3,6-dihydro-2H-pyran (Compound 9):

5 To a suspension of aluminum trichloride (2.67 g, 20 mmol) in dichloromethane (50 ml) was added 2-nitropropane (1.8 ml, 20 mmol) at 0 °C. At the same temperature, a solution of 2-methylbutanal (17.2 g, 200 mmol) and 2,3-dimethylbutadiene (24.6 g, 300 mmol) in dichloromethane (30 ml) was added dropwise with stirring, and stirring was continued at 0 °C for 30
10 min. and at room temperature for 2 h, prior to the addition of another portion of 2,3-dimethylbutadiene (24.6 g, 300 mmol). After further stirring at room temperature for 15 h, the reaction mixture was poured into water (300 ml) and the product was extracted with MTBE (3x 300 ml). The combined organic extracts were dried and concentrated under reduced pressure. The resulting
15 crude product was purified by distillation to provide at 90–92 °C / 20 mbar the title compound 9 (5.76 g, 17%).

Odor: Rose oxide, green, aromatic. – IR (neat): ν = 1099 cm⁻¹ (ν C–O–C), 1383 (δ CH₃), 1457 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.91 / 0.97 (2d, *J* = 7.0 Hz, 3H, 1'-Me),
20 0.92 / 0.93 (2t, *J* = 7.0 Hz, 3H, 4'-H₃), 1.15–1.64 (m, 3H, 1'-H, 2'-H₂), 1.56 / 1.67 (2s, 6H, 4-,5-Me), 1.77 (2 br. d, *J* = 16.0 Hz, 1H, 3-H_b), 2.05 / 2.08 (2 br. t, *J* = 16.0 Hz, 1H, 3-H_a), 3.30 (m, 1H, 2-H), 3.97 / 4.03 (2d, *J* = 15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 11.3 / 11.5 (q, C-3'), 13.7 / 13.8 / 14.2 / 14.6 (4q, 5-Me, C-4'),
25 18.4 / 18.5 (2q, 4-Me), 25.0 / 25.4 (2t, C-2'), 33.1 / 33.7 (2t, C-3), 39.2 / 39.3 (2d, C-1'), 70.1 / 70.2 (2t, C-6), 77.9 / 77.9 (2d, C-2), 123.7 / 123.8 / 124.4 / 124.4 (4s, C-4,-5). – MS (EI): *m/z* (%) = 41 (44) [C₃H₅⁺], 55 (59) [C₄H₇⁺], 67 (75) [C₅H₇⁺], 83 (100) [C₆H₁₁⁺], 111 (58) [M⁺–C₄H₉], 153 (2) [M⁺–CH₃], 168 (45) [M⁺].

30 4,5-Dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-pyran (Compound 10):

2-Nitropropane (1.8 ml, 20 mmol) was added at -10°C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, 2-methylpentanal (20.0 g, 200 mmol) was added dropwise during 20 min, followed by 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) 5 during 30 min. After further stirring at this temperature for 30 min, and for 1h at ambient temperature, the reaction mixture was poured into water (300 ml) and the product extracted with MTBE (3x 300 ml). The combined organic extracts were dried, concentrated in vacuo, and purified by silica-gel FC (pentane/MTBE, 100:1, R_f = 0.21) to provide the title compound 10 (7.43 g, 10 20%).

Odor: Green, vegetable, aromatic, tea-like. – IR (neat): $\nu = 1101\text{ cm}^{-1}$ ($\nu\text{ C-O-C}$), 1383 ($\delta\text{ CH}_3$), 1456 ($\delta\text{ CH}_2$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.88 / 0.94$ (2d, $J = 7.0\text{ Hz}$, 3H, 1'-Me), 0.89 / 0.90 (2t, $J = 7.0\text{ Hz}$, 3H, 4'-H₃), 1.10–1.61 (m, 5H, 1'-H, 2',-3'-H₂'), 15 1.52 / 1.64 (2s, 6H, 4-,5-Me), 1.73 (br. d, $J = 16.5\text{ Hz}$, 1H, 3-H_b), 2.05 (m, 1H, 3-H_a), 3.26 (m, 1H, 2-H), 3.94 / 4.00 (2 br. d, $J = 15.5\text{ Hz}$, 2H, 6-H₂). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 13.8 / 14.3 / 14.7 / 15.1$ (4q, 5-Me, C-4'), 18.3 / 18.4 (2q, 4-Me), 20.1 / 20.2 (2t, C-2'), 33.0 / 33.6 (2t, C-3'), 34.6 / 35.0 (2t, C-3), 37.3 / 37.5 (2d, C-1'), 70.1 / 70.2 (2t, C-6), 78.1 / 78.2 (2d, C-2), 123.6 / 123.7 / 124.4 / 124.4 (4s, C-4,-5). 20 – MS (EI): m/z (%) = 43 (44) [C_3H_7^+], 55 (55) [C_4H_9^+], 67 (67) [C_5H_7^+], 83 (100) [$\text{C}_6\text{H}_{11}^+$], 111 (63) [$\text{M}^+-\text{C}_5\text{H}_{11}$], 167 (2) [M^+-CH_3], 182 (30) [M^+].

Floral-green perfume oil for fabric softeners:

25

	compound/ingredient	parts by weight 1/1150
1.	Agrumex (<i>ortho-tert</i> -Butylcyclohexyl acetate)	5
2.	Aubepine (<i>para</i> -Methoxybenzaldehyde) / <i>para</i> -cresol	15
30 3.	Benzyl acetate	25
4.	Benzyl salicylate	35

5.	<i>para-tert</i> -Butylcyclohexyl acetate	106
6.	Butyl hydroxy toluene	2
7.	Cinnamic alcohol	5
8.	Citronellol, extra quality	50
5	9. Coumarine, pure, crystalline	10
10.	Damascenone @ 1% in DPG	10
11.	<i>alpha</i> -Damascone @ 10% in DPG	4
12.	<i>gamma</i> -Decalactone	4
13.	Decanal	4
10	14. Dihydromyrcenol	40
15.	DPG (Dipropylene glycol)	20
16.	Ebanol (3-Methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol)	3
17.	Ethyl vanillin	3
15	18. Eugenol, pure @ 10% in DPG	10
19.	Fixolide (6-Acetyl-1,1,2,4,4,7-hexamethyltetralin)	10
20.	Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	100
21.	Gardenol (1-Phenylethyl acetate)	15
20	22. Geraniol	40
23.	<i>alpha</i> -Hexylcinnamaldehyde	90
24.	6-/8-Isobutylquinoline @ 10% in DPG	5
25.	Isoraldeine 70 (8-Methylionone)	50
26.	Lilial (2-Methyl-3-(4- <i>tert</i> -butylphenyl)propanal)	80
25	27. Linalool	80
28.	Manzanate (Ethyl 2-methyl pentanoate) @ 10% in DPG	5
29.	Mayol (<i>para</i> -Isopropylcyclohexylmethanol)	2
30.	Menthone @ 10% in DPG	5
31.	2-Methyldecanal @ 10% in DPG	3
30	32. 6-Methylhept-5-en-2-one @ 10% in DPG	10
33.	Methyl isoeugenol	5

34.	Methyl salicylate @ 10% in DPG	5
35.	Nerol, extra quality	10
36.	Okoumal (2,4-Dimethyl-2-(1,1,4,4-tetramethyl-tetralin-6-yl)-1,3-dioxolane)	15
5	37. 2-Phenylethanol	25
38.	Strawberry pure (Ethyl 3-methyl-3-phenylglycidate) @ 10% in DPG	10
39.	Terpenyl acetate	40
40.	Terpineol, pure	70
10	41. <i>gamma</i> -Undecalactone	4
42.	Undecanal	40
43.	10-Undecenal @ 10% in DPG	20
44.	Verdyl acetate	30
45.	Veloutone (2,2,5-Trimethyl-5-pentylcyclopentanone) @ 10% in DPG	10
15	46. Ylang ylang oil	15
47.	Compound 5 @ 10% in DPG	5

1150

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Compound 5 conveys to this perfume freshness and lift, and in particular petigrain-type aspects. It combines very well with the aldehydes, and turns the top note of the fragrance oil more eau de cologne-like; thereby, 5 attenuates the functional aspects of the fragrance and the fabric softener 25 becomes overall more sophisticated, more refined.

Floral-marine fragrance for soap:

30	compound/ingredient	parts by weight 1/820
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1.	Agrumex (2- <i>tert</i> -Butylcyclohexyl acetate)	30
2.	Ambrofix (3-Methylidodehydro-6,6-9a- oxidotetranorlabdane) @ 10% in DEP	2
3.	Aubepine (<i>para</i> -Methoxybenzaldehyde)	
5	/ <i>para</i> -cresol @ 10% in DPG	2
4.	Bergamot Givco 104	80
5.	<i>iso</i> -Butyl benzoate	30
6.	Cassis Base 345-F CS	2
7.	Cetone V (1-(2,6,6-Trimethyl-2-cyclohexen-1-yl)- 10 hepta-1,6-dien-3-one)	2
8.	Citral	5
9.	Citron Ess Reconst 1385	10
10.	Citronellyl nitrile	1
11.	<i>beta</i> -Damascone @ 1% in DPG	20
15	12. 2,4-Dimethyl-3-cyclohexenecarboxaldehyde	4
	13. DPG (Dipropylene glycol)	83
	14. Floralozone (<i>alpha,alpha</i> -Dimethyl-4- ethylbenzenepropanal)	5
	15. Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl- 20 1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	30
	16. Geraniol, extra quality	5
	17. Hedione	100
	18. <i>cis</i> -3-Hexenol @ 10% in DPG	5
	19. <i>cis</i> -3-Hexenyl acetate @ 10% in DPG	5
25	20. <i>cis</i> -3-Hexenyl butyrate @ 10% in DPG	5
	21. <i>cis</i> -3-Hexenyl hexenoate @ 10% in triethyl citrate	10
	22. <i>alpha</i> -Hexylcinnamaldehyde	100
	23. <i>beta</i> -Ionone	15
	24. <i>cis</i> -Jasmone	2
30	25. Linalool	50
	26. Mandarinal Base (Firmenich)	3

27.	Methyl 2-nonyoate @ 1% in DPG	5
28.	Nerolidol	100
29.	Neroli oil	2
30.	Nutmeg (mace) oil @ 10 % in DPG	2
5 31.	Phenylethyl phenylacetate	3
32.	Terpenyl Acetate	50
33.	Terpineol, pure	20
34.	Terpinolene	10
35.	<i>gamma</i> -Undecalactone	2
10 36.	Compound 5 @ 10% in DPG	20

820

Compound 5 harmoniously combines the hesperidic, floral-marine and green notes of the fragrance; thereby, it rounds off the composition and increases its radiance. In addition, it introduces naturalness and increases the character of that fragrance. At this relatively high dosage, 5 brings as well facettes of petitgrain oil and jasmone in; overall, 5 conveys to the fragrance its unique texture, its fresh and hygienic but also soft and caressing character.

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Essai for a male fine fragrance:

	compound/ingredient	parts by weight 1/1000
25		
1.	Ambrein, pure Base (Biolande)	2
2.	Anise oil	2
3.	Artemisia (Armoise) oil	3
4.	Bergamotte Givco 104	80
30 5.	Benzyl salicylate	50
6.	Birch Leaf Givco 166	4

7.	Bornyl acetate	5
8.	Coumarine, pure	5
9.	Cyclal C (2,4-Dimethyl-3-cyclohexene carboxaldehyde)	1
10.	<i>delta</i> -Damascone	1
5	11. Dihydromyrcenol	120
	12. DPG (Dipropylene glycol)	95
10	13. Evernyl (Methyl 3,6-dimethylresorcylate)	8
	14. Fir balsam resinoide	2
	15. Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	180
10	16. Galbanone 10 (1-(5,5-Dimethyl-1-cyclohexen-1-yl)-4-penten-1-one)	5
	16. Gardenol (1-Phenylethyl acetate)	2
	17. Geranium oil	8
15	18. Hedione	150
	19. Iso E Super	160
	20. Kephalis (4-(1-Ethoxyethenyl)-3,3,5,5-tetramethylcyclohexanone)	15
	21. Lavandin Grossio oil	3
20	22. Linalool	40
	23. Melonal (2,6-Dimethylhept-5-enal) @ 10% in DPG	1
	24. Nutmeg (mace) oil	5
	25. Patchouli oil (iron free)	8
	26. Radjanol	40
25	36. Compound 5	5

1000

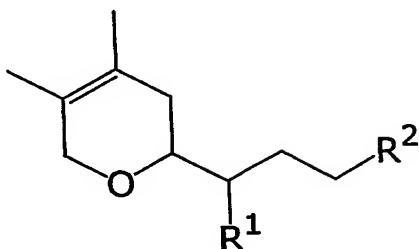
Compound 5 conveys to this male fine fragrance essai it's fresh facet: A green and invigorating botanical freshness, clean, clear and compelling. It enriches the classical top of this modern fougere by new aspects, increases radiance

30060P1

and diffusion, and harmonizes and stages the spicy accord of anise, artemisia and nutmeg oils. In result, this masculine scent acquires a herbal crispness that doesn't disturb the mysterious sensuality of the woody-musky-mossy-coumarine fond, but instead accentuates it.

Claims

1. A compound of the general formula (I)



or mixtures thereof,

wherein.

$R^1 = H, CH_3$ or CH_2CH_3 ,

$R^2 = H, CH_3, CH_2CH_3$ or $CH_2CH_2CH_3$,

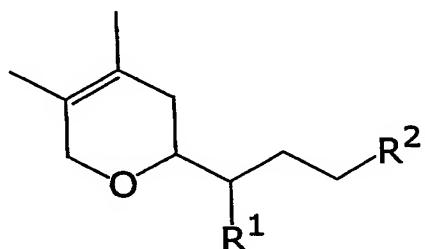
provided that when R^1 is H , R^2 is H .

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2. A compound according to claim 1 selected from the group consisting of
2-(1-ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-
propyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylpropyl)-3,6-
dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-
pyran; or mixtures thereof.

15

3. The use of a compound of the formula (I)



wherein,

R^1 is H, CH_3 , or CH_2CH_3 , and

R^2 is H, CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$

as a fragrance ingredient.

4. Use according to claim 3 wherein the compound is selected from the group consisting of 2-butyl-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-pentyl-3,6-dihydro-2H-pyran; 2-(1-ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran; 2-hexyl-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-propyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylpropyl)-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-pyran; or mixtures thereof.
5. A fragrance composition comprising a compound as defined in any of the claims 3 or 4, or mixtures thereof.

Abstract

Disclosed are 2,4,5-trialkyl-substituted 3,6-dihydro-2H-pyrans that are useful as fragrance ingredients, particularly in fine fragrances and functional perfumery.